Lee.

The Effect Of Ageing On The Constants Of Chinese Wood Oil.

THE EFFECT OF AGEING ON THE CONSTANTS OF CHINESE WOOD OIL

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Henry Rhodes Lee

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

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THE EFFECT OF AGEING ON THE CONSTANTS OF CHINESE WOOD OIL.

Chinese wood oil commonly known as "tung oil", has recently been made the subject of more research than any other drying oil. This seems natural when we consider the adaptability of this product as a base for paints and varnishes, as well as its peculiar chemical characteristics.

The oil is derived from the seeds of the trees, Aleurites Fordii[1] and Aleurites Montana[2],[3]. The former is grown on the heavy-clay hillsides above Hankow where the climate is similar to that of our Southern States; the latter is native to the southeastern parts of China. By far the greater part of the oil exported is derived from the Aleurites Fordii.

Considerable confusion in the literature on this subject has arisen through the indiscriminate use of the term "Tung oil." The Japanese wood oil or Aleurites Cordata has quite different analytical constants as compared with those of the previously mentioned species, yet it was not until 1910 that the distinction was recorded in the literature.[4]

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(1) Circular 108 U.S. Dept. of Agriculture. David Fairchild (1913)
(2) Wilson, Bull. Imp. Inst. London Eng. 2 No. 3 (1915)
(3) J. of Ind. & Chem. Eng. Vol. 8 No. 1 (1916)
(4) J. of Ind. & Chem. Eng. Vol. 2 205- (1910)

The Chinese wood oil tree commences to bear fruit when 4 or 5 years old. The fruits are about the size of small apples and contain 3 to 5 seeds, similar in shape to the Brazil nut. The valuable oil constitutes about 24% of the mass of the nuts.

The method of extraction of the oil is crude and the possibility of adulteration great. This results in considerable variation in the analytical constants. The seeds are roasted in large earthen dishes or iron pans over a free flame, ground to a powder, and then subjected to pressure in wooden presses.

The cold drawn oil is pale yellow in color and is called "pale" or white tung oil. The oil obtained by the hot pressing method is darker and has a low market value. This oil is consequently consumed in China while the white, marketable oil is exported. The oil is allowed to settle from six months to a year. It is then strained through coarse cloth and shipped to market in large bamboo baskets lined with varnished paper.

Chas. V. Bacon (5) who has investigated a large portion of the Chinese wood oil (34 percent in 1912) imported into this country in recent years, states that all the oil imported into the United States is derived from the species Aleurites Fordii and that the difference in constants is due to the methods of refining and marketing.

In the same discussion he states that the popular

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(5) Proceed. Am. Soc. Testing Materials XIII p. 944 (1913)

opinion that soya bean oil is the only adulterant found in Chinese wood oil is false. Peanut, rapeseed, teaseed, tallow-seed, linseed, fish oil, etc. which are all native to China and are made in and around Hankow, are common adulterants.

The bulk of the oil is exported from Hankow and Wuchow, 95% of it being exported from Hankow. In 1900, 21,960 tons of the white oil were exported from Hankow; in 1910, 50,338 tons were exported from the same port. These figures show plainly the increasing demand for this the most curious of vegetable oils.

Commercial Uses of Chinese Wood Oil:

In China, tung oil is used as a natural varnish, as a water proofing material, and as an illuminant. In this country it is used almost exclusively in the paint and varnish industries. It is the best drying oil known. Although less unsaturated than linseed oil it dries in one-third the time. A thin film of wood oil will become hard in twenty hours whereas a similar film of linseed oil requires 66 hours to attain the same degree of hardness.

It is used largely in the manufacture of rosin-wood oil varnishes; the product being superior in every way to the rosin-linseed oil varnishes.

Recent investigations on the analytical constants of commercial Chinese wood oil have shown it to be an extremely uniform product. The work of Kreikenbaum,(4) Chapman(6) and in the Contracts Laboratory(7) all bear out this assertion.

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(6) Analyst Vol. 37 p. 543 (1912)
(7) Proceedings 7th International Cong.App.Chem.Sec.1 (1909)p.89

Authentic samples of China wood oil investigated by the "oil committee" of the American Society for Testing Materials[8] also gave results indicative of the uniformity of commercial wood oil.

Chapman states, "There is no doubt that Chinese wood oil, like all other oils, varies within certain limits, both with respect to physical and chemical properties. As a matter of fact botanical and geographical origin, climatic variations, differences in treatment during the manufacture of the oil, and the duration and conditions of storage unquestionably affect its properties." Combined with these variable factors the effect of light and the ease of oxidation might be mentioned as additional factors as well as those changes induced by storage conditions and the ageing of the sample.

Composition of Chinese Wood Oil:

Chinese wood oil according to Lewkowitsch[9] consists primarily of the glycerides of oleic and eleomargaric acids. Eleo margaric acid is termed by him "an isomer of linolic acid".

Cloez[10] first isolated a crystalline easily oxidizable fatty acid from Japanese wood oil, to which he assigned the formula $C_{17}H_{30}O_2$ and which he called eleomargaric acid. He reported 24% oleic acid and 72% eleomargaric acid in Chinese wood oil. Eleomargaric acid was found to form a crystalline solid having a M.P. of 48°C. This acid when exposed to light formed a polymer B. eleostearic acid M.P. 72°C. It was also

(8) Proc.Am. Soc. Testing Materials XIII 1913 p. 923.
(9) Chem.Technology of Oils,Fats and Waxes. 1910
(10) Comp. Rend. 81: 469 (1875) 82 :501(1876) 83 :943 (1876)

stated that all their compounds with the exception of the potassium salt absorb oxygen rapidly.

Maquenne[11] repeated the experiments of Cloez and determined the formula as $C_{18}H_{30}O_2$ instead of $C_{17}H_{30}O_2$ as previously reported. By the oxidation with potassium permanganate he obtained n.-valeric acid and azelaic acid. He considered B eleostearic acid an isomer of eleostearic acid instead of a polymer.

M. Kitt[12] studied the gelatimization of Chinese wood oil and concluded that it was due to the formation of inner anhydrides. He also mentions the formation of B eleostearic acid by the action of light rays.

Morrell[13] concluded that polmerization results during the drying of an oil.

Kametaka[14] repeated the alkaline potassium permanganate oxidation proposed by Kitt and concluded that the solid acids which Cloez named elaeomargaric acid and for which Maquenne proposed the name A. elaeostearic acid has the formula $C_{18}H_{32}O_2$ and not $C_{18}H_{30}O_2$ as given by Maquenne. He also concluded that the solid acid formed was undoubtedly a steroisomeride of linolenic acid; the bromine addition product $C_{18}H_{32}O_2Br_4$ as well as the oxidation product $C_{18}H_{32}(OH)_4O_2$ agree with this conclusion. This demonstrated the presence of two double bonds instead of 3 as had been indicated by previous experimentation.

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(11) Comp. Rend 135:686 (1903) Jour. Chem. Soc. 83: 1042 (1903)
(12) Chem. Ztg. 23: 23 and 38 (1899)
(13) Jour. Chem. Soc. 101: 2082 (1912)
(14) Jour. Chem. Soc. 83: 1042 (1903)

Majima[15] using the ozone method of Harries[16] found that the elaeostearic acid took up two atoms of ozone; he therefore ascribed the formula $C_{18}H_{32}O_2$ to elaeostearic acid. As oxidation products he isolated n. - valeric acid or iso valeric acid $(CH_3)_2CH\,CH_2\,COOH$, n.- valeric aldehyde a half aldehyde of azelaic acid and azelaic acid $(CH_2)_7(COOH)_2$ He was not able to prove the presence of succinic acid, and it remained for Schapringer[17] using the ozone method of Harries to prove its pressure. This evidence proved conclusively the formula of Majima to be correct.

$$CH_3(CH_2)_3\,CH : CH\,(CH_2)_2\,CH : CH\,(CH_2)_7COOH.$$

The oxidation products leave no doubt as to the positions of the double bonds. Morrell confirms the formula of Majima and further states that this formula appears consistent with the fact that Chinese wood oil polymerizes on heating.

Fahrion[18] states that Chinese wood oil can become solid through two different processes; namely, through molecular change and through polymerization. The first process takes place at ordinary temperatures by the action of light and results in the formation of a crystalline solid. Both processes can take place in the absence of air. He concludes as a result of his work that the main constituent of Chinese wood oil is elaeomargaric acid.

Kametaka calculated elaeomargaric acid as 86 per cent of

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(15) Ber. 24: 674 (1909)
(16) Ber. 39:2844, 3728 (1906) 40: 4154, 4905 (1907) 41:1227(1908)
(17) Dissertation Karlsruhe 1912.
(18) Chemisches Centralblatt 83: 2154 (1912)

the oil and oleic acid 14 per cent. Boughton[19] reports an average of 90 per cent elaeomargaric acid calculating the weight of the potassium soap as equivalent to the weight of elaeomargaric acid.

The "Light Break."

It is a familiar fact that when Chinese wood oil is exposed to light it soon exhibits a white precipitate which gradually increases in amount until after a few months the oil may be entirely converted into a yellowish white solid mass. This change will take place by the action of light alone, in sealed glass tubes in an inert gas. To investigate this point five samples of wood oil were sealed in an atmosphere of nitrogen and exposed to the action of light. Along with these were placed duplicate samples loosely stoppered and exposed thereby to the atmosphere. Both series were placed in direct sunlight and were observed from time to time for differences in behavior. Solidification took place uniformly in the duplicate samples, though different periods of exposure were required for the different samples to form the solid product. It also became apparent that the solid glyceride separating on exposure to light acquired a lighter color under the influence of isolation than when exposed to the air. Since the glycerides themselves are colorless compounds it is evident that light and air together effect an oxidation of the impurities resulting in a change of color.

Ritsert[20] studied the effect of light alone on oils. He was led to the conclusion that when air is rigidly excluded, as

(19) Proceed. Am. Soc. Test. Materials 191 (1914)
(20) Ellis- Hydrogenation of Oils.

in the case of sealed tubes, even prolonged exposure to light is incapable of producing preceptible changes. It is altogether probable that such changes as the increase in acidity, leading ultimately to rancidity, are effected by the joint influences of light, moisture and air. The evidence is positive, however, that Chinese wood oil may become solid through the influence of light alone.

The white glyceride separating on exposure to light was recrystallized from acetone and was found to have a melting point of 60°C. This glyceride was separated by Morrell (21) into steroisomerides B. elaeostearic acid M.P. 72°C and A elaeostearic acid M.P. 48°C. These glycerides are very susceptible to oxidation; a sample of the mixed glycerides which gave an iodine number of 102 when first recrystallized from acetone, gave after two months of storage in a vaccum dessicator, an iodine number of 39.5 and changed in color from pure white to a deep yellow due to the oxidation of the contained impurities. It is quite possible that some oxidation had taken place before the initial analysis could be made.

This solid product formed by the action of light on Chinese wood oil has come to be designated as the "light break." This so-called "light break" is characteristic of wood oil alone and has served to introduce some unique tests for its purity.

Messrs. Ware and Schumann (21) have made use of this phenomenon in working out quantitative methods for the estimation of Chinese wood oil. They made use of certain catalytic agents

(21) Proceed. Am. Soc. Test. Materials 14: 455 (1914)

such as iodine, hydrogen iodide, sulfur chloride, carbon dioxide, hydrogen sulfied, phosphorus tri-bromide and carbon disulfide to accelerate the reaction and thus make it rapid enough for a laboratory method. Recent work by the same authors prove the tests inapplicable for commercial purposes as the factors of temperature and concentration must be too rigidly observed in order to obtain corfect results. The iodine jelly test investigated by the same committee did not appear any better as the gelatinization by iodine in chloroform is greatly retarded by the presence of small amounts of alcohol. This being the case, it seems plausible to think that the failure to gelatinize of Chinese wood oil which has long been exposed to the action of light, may be due to the tribasic alcohol liberated by the hydrolysis of the ester. Investigation of this point, however, proved conclusively that this is not the case, for when equimolecular quantities of glycerol and of the fatty acid separated on saponification of the ester were heated at the polymerization temperature, there was a resynthesis of the ester, resulting finally in polymerization and reduction of the initially high acid value to zero. A new method worked out by Ware (22) involving the optical dispersion of Chinese wood oil is claimed to be both rapid and accurate.

Polymerization of Chinese Wood Oil

Another peculiar characteristic of Chinese wood oil is its ability to polymerize with heat. So uniform is this reaction that it is capable of standardization and has become the most generally used test for purity and general adaptibility of the oil to the

(22) J. Ind. & Eng. Chem. 8 2 127 (1916)

to the requirements of the paint and varnish industries. The literature is filled with contradictory statements regarding the cause and mechanism of this reaction. Cloez[23] observed that there was a decrease of iodine number from 163 in the original oil to 107.7 in the polymerized product. Zucker[24] and Norman[25] both bear out the statement of Cloez in this particular. It was also observed by Cloez that a slight increase of saponification equivalent took place during the polymerization process. Shumann[3] has made a systematic study of this reaction and reports that "upon heating to a sufficiently high temperature two elaeomaragaric acid triglyceride molecules unite through the dissolution of one-half their double bonds, as is evidenced by their molecular weights and iodine numbers." The analysis of the triglyceride separated by repeated extraction with hot alcohol and extra light petroleum ether gave an iodine number of 85.5 and a molecular weight of 1692 - 1730, showing conclusively that half the double linkages have disappeared and that the molecular weight of the triglyceride is twice that of the original elaeomargaric triglyceride.

Scope of the Present Work.

Chinese wood oil being highly unsaturated as well as susceptible to photochemical reactions on exposure to light is subject to more change on ageing than any other drying oil. This research was begun with a view to determine the extent of this

(23) Chem. Ztg. 30: 865 (1906)
(24) Pharm. Ztg. 43: 628 (1898)
(25) Chem. Ztg. 31: 188 (1907)

change.

The value of this work depends partly on the fact that the samples whose constants were determined were carefully taken and are representative, as well as the fact that the first series is composed of the identical samples collected and worked on by A. Kreikenbaum in 1907-1908. This series has, therefore, been under observation eight years and the most important analytical constants have been twice redetermined.

These samples after Mr. Kreikenbaum's preliminary work had been completed, were sent to the University of Illinois with the request that further investigation of them be made.

In 1913 C.L. Monroe took up the work and redetermined the constants of the first series comparing them with those of a new set of samples collected from reliable sources. His results though unpublished are to be found in thesis form in the University of Illinois library.

The work has been continued during the present year by the author and the redetermined constants of both of the above series have been compared with those of a third set of samples freshly collected.

A brief history of the samples while in storage will explain to some extent the changes brought about by ageing. Previous to the time when Monroe began his investigation the Kreikenbaum samples, which shall be designated as Series I, were used as museum samples, being subjected to the influence of light as well as small amounts of air and moisture admitted by occasionally opening the sample bottles for purposes of comparing the properties of the

different oils. Since Monroe finished his investigation both sets of samples have been stored in a dark cool cupboard near the floor. They were not opened again until this year when the present work was begun.

The following brief table will serve to differentiate the samples and give some idea of the condition of storage, age of the samples, etc.

TABLE I.

Sample No.	Date	Age	Colour	Number of Barrels taken from	Received from	Color of bottle	Kind of stopper
1.	Oct.'08		light	100	Kreikenbaum	dark	cork
2.	" '07		"	100	"	"	"
4.	" '07		"	20	"	"	"
5.	Sept "		dark	88	"	"	glass
7.	Oct.'08		light	100	"	"	cork
8.	June'09		"	249	"	light	"
9.	" "		dark	200	"	"	"
10.	" "		"	500	"	"	"
100.	Mar.'13	7 mo.	light	10	Patterson, Boardman & Knapp	dark	"
101.	" "	"	"	20	L.C.Gillespie & Sons	"	glass
102.	" "	"	"	300	G.W.S.Patterson & Co.	"	"
103.	" "	"	"	1	Edw. Hill's Son & Co	"	"
104.	" "	"	"	100	Marden, Orth, and Hastings	"	"
201.	Nov.'15		Pale		Mitsui & Co	light	cork wax sealed

Sample No.	Date	Age Colour	Number of Barrels taken from	Received from	Color of bottle	Kind of stopper
202	Nov. '15	Pale	--	Mitsui & Co	Light	Cork wax seald
203	"	"	--	"	"	"
204	"	"	290	S.Winterbourne & Co.	Can	---

This opportunity is taken to acknowledge the courtesy of Mitsui & Company, New York City and S. Winterbourne & Company also of New York City who so very generously and promptly responded to the request for a representative sample of Chinese wood oil.

General Effects of Ageing.

The characteristic changes experienced by most oils on exposure to light, air and moisture are; an increase in specific gravity, index of refraction and temperature reaction with sulfuric acid, with a corresponding decrease in iodine absorbtion value. An increase in acidity may or may not occur.

Sherman (26) states that age alone probably has no appreciable effect upon the analytical constants of commercially pure fatty acids, but when kept for a considerable length of time in contact with the air in partially filled or losely stoppered vessels they take up atmospheric oxygen and gradually become changed in those properties commonly known as constants. What is true of free fatty acids is likewise true to a large degree of the glycerides of these acids. Chinese wood oil being a glyceride of a highly unsaturated fatty acid is very sensitive to light

(26) Sherman's Organic Analysis p. 210

and undergoes a characteristic photochemical reaction which not only alters its physical properties but its chemical properties as well. The speed of this reaction depends entirely on the nature and intensity of the light. Ultra violet light hastens the change but ordinary glass is not penetrated by the ultra violet ray. Storage in brown bottles shuts out part of the light and decreases the rate of this change. Four samples stored in brown bottles under identical conditions with four other samples stored in light bottles gave no evidence of the "light break" on continued exposure. The samples stored in light bottles all gave the "light break" within six months' exposure.

Determination of the Iodine Number.

Kreikenbaum[4] in his investigation made a comparative study of the applicability of the Hübl and Hanus methods to Chinese wood oil. His results prove the Hanus method inapplicable. Chapman[7] prefers the Wijs method, stating that concordant results can be obtained when all the conditions of time of absorbtion and temperature are carefully observed. Kreikenbaum states that a six to seven-hour absorbtion period will suffice but that it is better to use the standard 18-hour absorbtion. He reports as an average of all Hübl absorbtions between 4 and 20 hours, 170.4. Chapman gives as the average of 17 determinations by the Wijs method 170.6.

The following results were obtained in this laboratory using the Hübl method and an 18 to 24 hour absorbtion period.

TABLE II.

DETERMINATION OF IODINE NUMBER.

Sample No.	Date of Determinations. 1908	1913	1915
1	170.2	167.	167.5
2	170.6	163.4	164.3
3	170.3	----	----
4	170.4	165.4	164.5
5	172.8	169.9	164.3
6	170.1	----	----
7	170.1	169.3	164.3
8	170.7	168.1	167.2
9	171.6	169.2	169.2
10	171.6	168.5	166.1
Average	170.8	167.6	166.
100		170.2	167.3
101		170.8	168.7
102		171.2	169.3
103		170.	169.6
104		170.2	(156.5) Solid
Average		170.5	168.7
201			170.9
202			172.4
203			(164.5)*
204			170.9
Average			171.4

*Oil 203 had undoubtedly aged or had been adulterated as it also gave a high saponification equivalent.

These figures represent in every case the average result of at least 3 check determinations. It is to be observed that a gradual decrease in iodine number has taken place in every sample. The abnormal lowering of iodine number in the case of sample 104 is to be explained by the fact that this container had been placed near a steam pipe and the oil had been slowly polymerized by heat. The oil had become completely solid and it required the temperature of the steam bath to bring it back into the fluid condition. The decrease of iodine value is to be attributed to the process of natural oxidation. It is probable that the only difference between artificial oxidation with alkaline potassium permanganate or ozone and natural oxidation by the air is one of degree rather than kind. It is probable also that all of the unsaturated fatty acids having 18 carbon atoms are subject to this slow or natural oxidation process when exposed to the air in either partially filled or loosely stoppered containers. Light alone will cause a decrease in the iodine number through the dissolution of the unsaturated linkages by union with other molecules of the same kind. The oils as shown by table No. 2 have shown an average change of iodine number from 171 to 166.

Determination of the Saponification Number.

The method recommended by Sherman (26) was used for the determination of the saponification number. The results of all determinations on this constant are presented in table III.

Reference 26. page 144.

TABLE III

SAPONIFICATION NUMBER

Sample No.	Date of Determination 1908	1913	1916
1	191.8	192.5	195.2
2	190.2	194.6	195.0
3	191.8	-----	-----
4	190.7	194.9	195.6
5	191.3	195.7	196.4
6	191.7	-----	-----
7	190.6	195.7	195.2
8	189.8	195.2	196.5
9	190.5	192.0	196.0
10	190.6	192.2	196.9
Average	190.9	194.1	195.2
100		190.3	196.1
101		190.0	193.9
102		190.8	196.5
103		191.5	195.2
104		190.7	Polymerized
Average		190.6	195.4
201			190.2
202			191.0
203			197.2
204			190.
Average eliminating No.103			190.4

The table shows a gradual increase of saponification number on ageing. The average for the ten oils in the first series in 1908 was 190.9. Mr. Monroe working on these same samples in 1913 obtained 194.1 as an average of eight of this series. The present investigation shows an increase to 195.2. The samples of series two have undergone an average change of from 190.6 to 195.4. The fresh samples (1915) gave 190.8 as an average result. It was shown by Majima that azelaic acid is a product of the artificial oxidation of elaeomargaric acid triglyceride. It has been shown by Nicolet (27) and Liddle that it is also a product of the natural oxidation of glycerides of the oleic, linolic and linolenic series. They found in the case of oxidized linseed oil that only one-eighteenth of the total azelaic acid existed as free acid. Saponification rendered the rest of the available acid soluble and it was reasoned from this that the larger part of the acid must exist as the glyceride. This statement is also borne out by the fact that many oils maintain an almost constant acid number while the saponification number constantly increases with age. If, as hasalready been stated, the general effect of ageing is to decrease the iodine number through slight oxidation, it seems probable in view of the modern explanation of acidity that a small amount of the triglyceride might be oxidized to the point where the chain would break with the formation of new acids. This of course would result in an increase in the number of carboxyl groups and cause a corresponding increase in the saponification number. The

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(27) Jour. Ind. Eng. Chem. 8 No. 5 416 (1916)

saponification number of linolein is 191.7 and as Chinese wood oil is composed, 90% of an isomer of this glyceride, it is not surprising that three different investigators working at widely separated intervals of time should obtain average results so closely in agreement as 190.9, 190.6 and 190.8. It is also a proof for the uniformity of Chinese wood oil over a considerable period of time.

Determination of the Acid Value.

It should be noticed at the beginning that the acid number is the only constant which varies greatly in the fresh oil. There is apparently not a great deal of difference in this property in oils that have been freshly extracted although considerable acidity may develop in the seeds before the oil is expressed. Results on this constant shown in table IV range from an initial acidity of 1.7 to 7.1. It is to be observed also that those samples having a high initial acidity have become more acid in a given interval of time than those having a low initial acidity. This would indicate that the reaction resulting in the production of rancidity is catalyzed by the presence of the organic acids liberated by the hydrolysis. This is to be expected since the presence of an acid greatly accelerates hydrolysis. The production of acidity is due to a slow hydrolysis or oxidation and may be accelerated either by the presence of an acid or by the natural fermenting enzymes of the fresh oil.

TABLE IV

ACID NUMBERS

Sample No.	Date of Analysis 1908	1915	Difference
1	4.8	7.1	2.3
2	2.3	4.1	1.8
3	3.3	---	---
4	1.7	3.3	1.6
5	4.5	6.5	2.
6	5.3	---	---
7	6.1	8.3	2.2
8	7.	10.4	3.4
9	7.1	9.0	1.9
10	2.4	4.2	1.8
Average	4.5	6.6	
100		3.3	
101		6.5	
102		7.0	
103		5.6	
104		(11.5) (solid)	
Average		5.8	
201		3.7	
202		7.5	
203		2.9	
204		3.3	
Average		4.3	

Specific Gravity

The specific gravity of Chinese wood oil is higher than that of most of the common fixed oils. Kreikenbaum[4] gives .9405 as the minimum figure at 15.5°C. He also states that exposure increases the specific gravity of an oil. Chapman[6] states that a specific gravity below .940 is cause for suspicion. There is, however, no published data to show that oils of low specific gravity are not suited for use in varnish. Table V shows the constants of the oils used in this investigation. There has been a gradual increase of this constant on ageing showing that either certain volatile compounds of lower specific gravity were formed and distilled off or that some intermolecular change resulting in a decrease in volume must have taken place. The specific gravity is not greatly influenced by the appearance of the "light break."

TABLE V.

SPECIFIC GRAVITY.

SAMPLE NO.	DATE OF ANALYSIS 1908	1915	SAMPLE NO.	DATE OF ANALYSIS 1908	1915
1	.9419	.9431	100		.9400
2	.9430	.9441	101		.9416
3	.9436	----	102		.9424
4	.9454*	.9458	103		.9410
5	.9413	.9414	104		solid
6	.9411	.----			
7	.9405	.9453	201		.9380
8	.9413	.9489	202		.9372
9	.9413	.9476	203		.9379
10	.9412	.9445	204		.9401
Average		.9452			

*Exposed to air for two years.

Refractive Index.

Ageing ordinarly causes an increase in the refractive index of an oil. Kreikenbaum did not determine this constant but it was later determined by Monroe on the same series of samples and gave 1.5173 as an average result. This constant as shown in table VI has experienced a gradual increase. The samples obtained this year, however, gave a refractive index higher than those which had aged, indicating that the first change has been in the direction of a decided decrease in refractive index accompanied by a gradual rise on further exposure.

Chapman (7) states that a refractive index of less than 1.515 at 20°C is suspicious. The specific refractive power (28) is also shown in table VI but no comparative data is at hand since the specific gravity of the samples was not determined in 1913 and the refractive index was not recorded in 1908.

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(28) Ber. No. 15 , 1031 (1882) Calculated from Landolt's formula $\frac{N-1}{D}$ in which N is the index of the fraction and D is specific gravity.

TABLE VI

REFRACTIVE INDEX AND SPECIFIC REFRACTIVE POWER.

	Specific Gravity		Specific Refractive Power
	Date of Determination		
Sample No.	1913	1916	1916
1	1.5175	1.5191	.5504
2	1.5176	1.5211	.5511
4	1.5178	1.5215	.5513
5	1.5170	1.5194	.5510
7	1.5173	1.5178	.5477
8	1.5172	1.5189	.5468
9	1.5171	1.5188	.5475
10	1.5171	1.5192	.5409
Average	1.5173	1.5195	.5481
100	1.5169	1.5190	.5521
101	1.5169	1.5192	.5517
102	1.5168	1.5191	.5509
103	1.5168	1.5194	.5511
Average	1.5168	1.5192	.5514
201		1.5217	.5561
202		1.5218	.5567
203		1.5166	.5501
204		1.5210	.5541
Average		1.5203	.5542

Hydrogenation Experiments.

The instability of Chinese wood oil together with its high degree of unsaturation led to a series of experiments with a view to hydrogenation. It was thought possible to greatly increase the speed of the reaction resulting in the formation of the "light break" by the catalytic action of ultra violet light.

Observations on the catalytic action of ultra violet light in the presence of platinum have been made by Farmer and Parker (29) indicating that ultra violet light has a retarding influence on colloidal platinum. No direct action of chemically active rays has been recorded.

Action of Ultra Violet Light on Chinese Wood Oil.

Hydrogen prepared by the action of Hydrochloric acid on zinc was purified by passing through a train of sulphuric acid and Potassium permanganate and finally passing the dry hydrogen through two oil containing recepticles, the one of glass, the other of quartz, connected in series. A 15 gram sample of wood oil was placed in each of the containers and the same was exposed to the rays of a Cooper Hewitt mercury vapor light. The lamp was allowed to run for one hour and the amount of hydrogenation taking place was observed from the decrease in iodine number of the samples. The following data shows quite an appreciable hydrogenation in the quartz tube while the sample in glass was unaffected.

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(29) Ellis Hydrogenation of Oils.

Iodine Numbers Before Hydrogenation.

167 168

Iodine Number after Hydrogenation in glass tube.

167.2 166.6

Iodine Number after Hydrogenation in Quartz tube.

156.7 157.

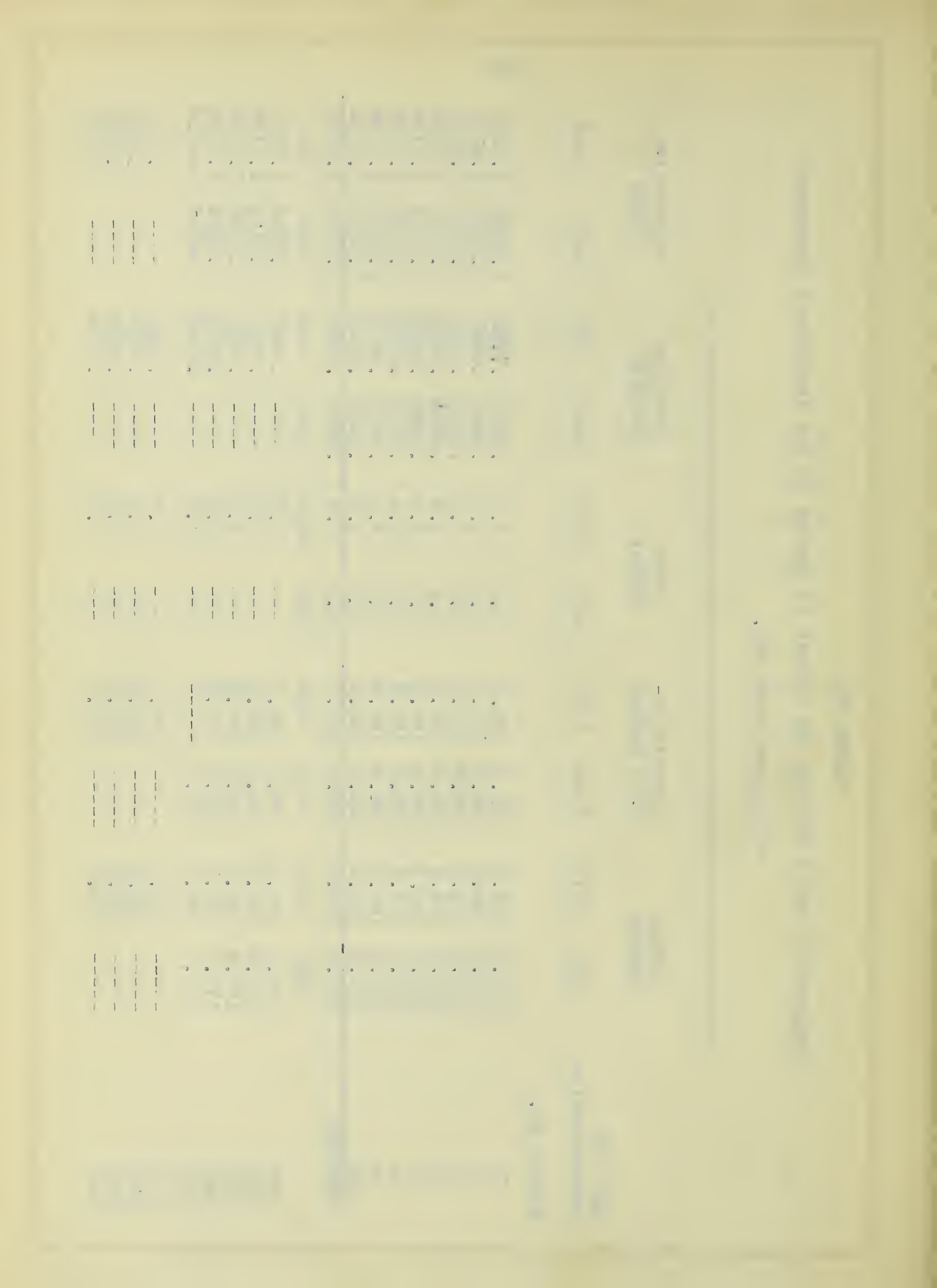
A yield of 6% of the hydrogenated product as calculated from the Iodine number was obtained. Hydrogenation of Chinese wood oil could not be carried out in the presence of a catalyst requiring high temperatures to increase its activity as wood oil itself is readily polymerized by heat.

The value of wood oil in the paint and varnish industries as well as its poisonous nature would preclude its use as a lard substitute even though it is easily hydrogenated. This experiment was carried out with a view to catalize the formation of the "light break". The reaction, however, is too slow to be of any value as an analytical test.

TABLE VII

Comparative Table Showing the Effect of Ageing on the Analytical Constants of Chinese Wood Oil.

	Iodine Number		Saponification Number		Acid Number		Specific Gravity		Refractive Index	
Date of Determination	1908	1915	1908	1915	1908	1915	1908	1915	1913	1916
Sample No.										
1	170.2	167.5	191.8	195.2	4.8	7.1	.9419	.9431	1.5175	1.5191
2	170.6	164.6	190.2	195.0	2.3	4.1	.9430	.9441	1.5175	1.5216
4	170.4	164.5	190.7	195.6	1.7	3.3	.9454	.9458	1.5178	1.5215
5	172.8	164.3	191.3	196.4	4.5	6.5	.9414	.9424	1.5170	1.5194
7	170.1	164.3	190.6	195.2	6.1	8.3	.9405	.9453	1.5173	1.5178
8	170.7	167.2	189.8	196.5	7.0	10.4	.9413	.9489	1.5172	1.5189
9	171.6	169.2	190.5	196.0	7.1	9.0	.9413	.9476	1.5171	1.5188
10	171.6	166.1	190.6	195.9	2.4	4.2	.9412	.9445	1.5171	1.5192
Average	171.0	166.0	190.0	195.7	4.5	6.6	.9421	.9452	1.5173	1.5195
	1912	1915	1912	1915	1908	1915	1908	1915	1913	1916
100	170.2	167.3	190.3	196.1	---	3.3	----	.9400	1.5169	1.5190
101	170.8	168.7	190.0	193.9	---	6.5	----	.9416	1.5169	1.5192
102	171.2	169.3	190.8	196.5	---	7.0	----	.9424	1.5168	1.5192
103	170.0	169.7	191.5	195.2	---	5.6	----	.9410	1.5168	1.5194
104	170.2	156.5	190.7	-----	---	11.5	----	solid	solid	solid
201	-----	170.9	-----	190.2	---	3.7	----	.9380	----	1.5217
202	-----	172.4	-----	191.0	---	7.5	----	.9372	----	1.5218
203	-----	164.5	-----	197.2	---	2.9	----	.9372	----	1.5216
204	-----	170.9	-----	190.0	---	3.3	----	.9372	----	1.5216



A comparative study of table VII shows the effect of ageing on the more important analytical constants of Chinese Wood oil, and points to the following conclusions:

(1) That the Chinese wood oil of commerce is an exceedingly uniform product.

(2) When exposed to small amounts of air and moisture, wood oil experiences a normal oxidation which results in a very appreciable decrease in iodine number. The average decrease in iodine number of 8 samples which have been under observation 7 years was from 171 to 166.

(3) The saponification number of this same series during the same period of exposure has undergone an average increase of from 190.9 in the initial analysis to 195.7 in the final analysis.

This increase in saponification number is to be attributed to the complete oxidation of a part of the oil resulting as in the case of artificial oxidation in the formation of decomposition acids, probably identical with those formed by artificial oxidation with alkaline permanganate.

(4) The acidity of every sample has been slowly increased by ageing. This may be attributed either to the hydrolysis of the ester or to oxidation resulting ultimately in the formation of new acids.

(5) The specific gravity has also been subject to a gradual increase under the conditions of this experiment. Apparently this is brought about by imter-molecular processes which result in a decrease in volume. It is also possible that substances of comparatively low specific gravity slowly distill

off leaving the residual oil with a slightly higher specific gravity.

(6) It is apparent that the specific gravity and refractive index are somewhat inter-dependent. It is obvious that a change of specific gravity not caused by inter-molecular changes would affect the refractive index by direct ratio. This fact must be made use of if any value is to be attached to the determination of the specific refractive power.

(7) Chinese wood oil must be fresh in order to yield comparable analytical constants. Many of the erratic results reported in the literature may be attributed primarily to the failure to observe this fact.

(8) Chinese wood oil is more susceptible than any other drying oil to photo chemical reactions.

(9) The speed of the formation of the "light break" is dependent on the nature and intensity of the light and may be greatly hastened by the catalytic influence of ultra violet light.

(10) Wood oil is readily hydrogenated and hydrogenation may likewise be catalyzed by the action of ultra violet light.